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Measurement of Stratospheric Chlorine Monoxide and Other Trace Constituents From a Portable Ground-Based mm-Wave System

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In 1976, the Astronomy Program and Physics Department at the State University of New York at Stony Brook started a joint research project to develop a ground-based millimeter wave receiver capable of detecting and measuring thermal emission from the rotational lines of chlorine oxide and other stratospheric trace constituents. During the period 1982 to 1989 this research was supported by the above grant. The emphasis throughout the project was on measuring the mixing ratio and altitude distribution of chlorine oxide, ClO, which is directly involved in, and is the single most important tracer of, the catalytic destruction of ozone [1]. This period was marked by very successful **measurements of vital importance to understanding the ozone depletion problem, including the first strong evidence that the Antarctic ozone hole is caused by man-made Chlorofluorocarbons.**

In addition to the principal investigators, this experiment was carried out by Alan Parrish, who played a vital role in designing the instrument and obtaining data, and Jim Barrett, who was primarily responsible for most of the data reduction and analysis software. Barrett and Parrish were involved over the entire length of the project. Important contributions were also made by M. Jaramillo and B. Connor.

The first successful detection of ClO from the ground was made from our observing station in Massachusetts during the winter of 1979–80 [2]. During the period October–December, 1982, we moved the experiment to Mauna Kea, Hawaii, to take advantage of the good site, and with an improved mixer succeeded in obtaining high quality ClO spectra around the clock, demonstrating the diurnal variation of ClO [3], an important test of the photochemistry. During the period 1982–86, a series of observations from Mauna Kea established a data base for long-term trends in ClO.

We also made observations of several other trace species of significance in the stratosphere. A unique measurement of the profile of HO_2 above 35 km was established [4], and doubt was cast on the correctness of previous measurements which had indicated relatively high mixing ratios for this species in the 20–30 km range. (Those previous measurements were later shown indeed to be incorrect.) We also measured the vertical profile of N_2O above balloon-flight limits, and were able to make a significant comparison with theoretical profiles and with somewhat discrepant satellite measurements [5]. A measurement of the vertical profile of HCN was also made [6], showing that it was in substantial disagreement with theory, and this has been borne out by subsequent observations by other techniques. Several emission lines of ozone were measured, and seasonal changes in the vertical profile noted [7], and an upper limit was set for the mixing ratio of H_2O_2 in the middle stratosphere [8].

In 1986, following the discovery of the Antarctic ozone hole, we took the millimeter wave instrument to Antarctica as part of the National Ozone Expedition (NOZE). During September 1986, we discovered that the amount of ClO in the lower stratosphere above Antarctica, at the same time and altitude at which that the ozone depletion was taking place, was a hundred times greater than normal [9,10], demonstrating that the cause of the ozone depletion was chlorine from man-made chlorofluorocarbons. In the Antarctic spring of 1987, the experiment returned to Antarctica with a wider bandwidth spectrometer and succeeded in deriving the altitude profile of ClO from the spectrum, showing that both the rate and altitude range of ozone depletion could be accounted for by chemical depletion mechanisms [11,12]. A summary of this research is found in reference 13. Below we include some highlights of the research particularly with regard to the Antarctic ozone hole.

1986 National Ozone Expedition

In 1985, English researchers reported [14] that ozone over Halley Bay, Antarctica, during the austral spring had been declining drastically over the period 1960 to 1984. They showed that in October between the late 1960's and 1984 the total ozone column declined by about 40 percent. This discovery was soon confirmed [15] by records from the satellite Total Ozone Monitoring System, which failed to discover the low Antarctic ozone due to a data analysis algorithm which ignored very low readings. This startling result produced a variety of *ad hoc* explanations which fell into two main categories, chemical theories involving chlorine and dynamical theories involving vertical and/or latitudinal transport. In response to this Antarctic "ozone hole", an expedition to the American base at McMurdo Station, run by the National Science Foundation, was quickly organized for austral spring 1986, and became known as the National Ozone Expedition or NOZE. The Stony Brook millimeter wave instrument was used to measure chlorine monoxide, ozone and N_2O in the stratosphere as part of the expedition, which also included infrared and ultraviolet remote sensing instruments and balloon-borne ozone measuring instruments. The key to deciding between chemical and dynamical theories lay in the detection of large quantities of ClO by the millimeter wave instrument. The expedition arrived in Antarctica at the end of August 1986, just as the sun was reappearing and photochemistry beginning.

The balloon-borne ozone measurements [16] showed that the depletion of ozone was occurring in the *lower* stratosphere below 22 kilometers. The low altitude of the depletion layer presented a challenge to our instrument since a signal from this relatively high pressure region would produce a spectrum with very broad (in frequency) line wings, much harder to measure than the narrow spectrum of "normal" ClO. Data were taken around the clock from 1 September to 29 October; at the beginning of this period the sun was above the horizon for 10 hours a day, and for 24 hours per day after 11 October.

The Antarctic ClO spectra [9,10] were unlike any we had seen in the previous 6 years of measurement. Upon returning to Stony Brook in November,1986, comprehensive data analysis, using the nighttime spectra as a background to be subtracted as in the Hawaii diurnal cycle measurements, showed that the daytime spectra of ClO had very broad and strong line wings. The total integrated intensity out to the edge of the 256 MHz bandpass was 10 times greater than for a normal spectrum and the line wings extended out beyond the edge of the bandpass. The line wings, clear evidence of huge quantities

of low altitude ClO, showed both a diurnal variation and a secular change, decreasing during the latter half of September and disappearing by early October.

We investigated the altitude distribution of the ClO responsible for the early September emission by deconvolving the pressure broadened spectral line profile using two different mathematical techniques. The results of many numerical experiments with a wide array of starting profiles for the mixing ratios show that (1) the retrieved altitude profile is always bimodal with one maximum near 20 km and another at ~40 km, and (2) it was not possible, given the limited bandwidth of our instrument, to determine the precise shape of the lower stratospheric ClO profile. We could determine that there was substantial ClO below 25 km with a mixing ratio in the range of 0.5 to 1.5 ppbV, and that the average mixing ratio for ClO in the layer below 22 km., where ozone was being depleted was 1.5 ppbV [9,10]. This is more than 100 times greater than expected from "normal" ClO chemistry and clearly demonstrated that chlorine chemistry was responsible for the Antarctic ozone hole. Hofmann *et al.* [16] found most of the ozone depletion below 20 km over McMurdo occurring during the same time span as these observations. Thus the peak of the ClO in September coincides with the actual ozone loss.

In 1986, several competing theories on the causes of the ozone hole had been proposed and were still in contention. Other observations that we made helped to rule these out. First, our measurements [17] of the vertical profile of N_2O (the first ever made in the Antarctic winter vortex) showed a far stronger lapse rate with altitude than previously suspected. This can only be explained by significant downward motion during the winter months, with the N_2O remaining depressed throughout the austral spring. This ruled out a class of "upwelling" theories which attempted to explain the hole as a result of upward transport of ozone-poor air from the troposphere or low stratosphere. Second, our unique measurement of the ozone mixing ratio in the 30–55 km altitude range throughout the period when the ozone hole was developing [18] established that ozone depletion was certainly confined to the lower stratosphere, and could not be explained by the downward transport of NO, for instance.

Our 1986 measurements of extremely high ClO, more than 1 ppbv in the lower Antarctic stratosphere, were confirmed during the next year by both our own and airplane measurements during the spring of

1987 National Ozone Expedition

In preparation for a return to Antarctica we added a second 256 MHz filter bank giving the spectrometer a total bandwidth of 512 MHz. Very high quality data were obtained during the third week of September. These spectra with their greater bandwidth enabled us to determine the altitude distribution of ClO between 16 and 45 km (Figure 1). The bi-modal nature of the distribution and the huge ClO layer between about 16 and 22 km are basically the same as shown by our 1986 measurements, but the upper altitude limit of the 16–22 km layer was better defined, as was the peak occurring at 18 km. Table 1 presents the ClO mixing ratio and density in the lower stratosphere. Our data provide the only ClO altitude distribution over Antarctica obtained by any

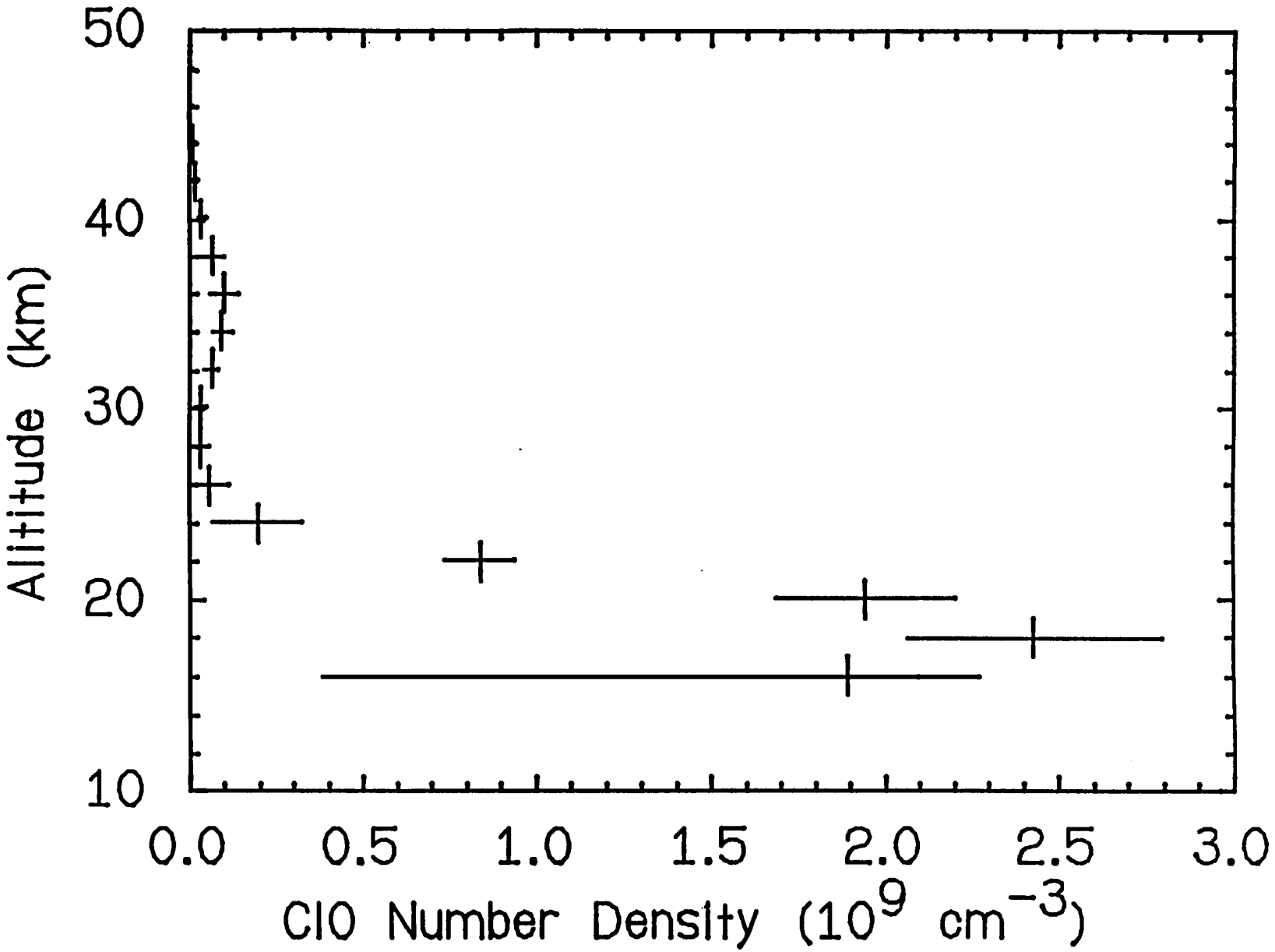

Figure 1: Midday number density altitude profile of ClO over McMurdo Station, Antarctica, during September 20–24, 1987, obtained by deconvolving spectra taken with the Stony Brook Millimeter Wave Spectrometer.

Table 1.

Daytime ClO over McMurdo Station, Antarctica, September 1987. Daytime is taken to be from 2 hours after stratospheric dawn to 2 hours before stratospheric sunset. Quoted errors in ClO mixing ratios are one standard deviation errors from the calibration of the millimeter-wave ClO measurements and profile retrieval. Percentage errors in [ClO] are the same as in the mixing ratio.

Altitude (km)	ClO mixing ratio (ppbV)	[ClO] (10^9 cm^{-3})
15–17	$0.6^{+0.09}_{-0.25}$	1.8
17–19	1.1 ± 0.15	2.3
19–21	1.3 ± 0.18	1.9
21–23	0.8 ± 0.11	0.9
23–25	0.3 ± 0.09	0.2

technique, and the only measurements above 18 kilometers. It is vitally important for understanding the ozone depletion problem.

Our analysis of the ClO profile compared with the ozone loss rate demonstrated quantitatively [11,12] that chlorine could be responsible for the ozone loss over Antarctica, *via* a mechanism involving the formation of ClO dimers [19].

Following our second season of measurements in Antarctica, a significant effort was put into making further improvements in the performance of the Stony Brook mm-Wave Spectrometer. This effort consisted of a revision of the quai-optical local oscillator injection system, and an enlargement of all mm-wave mirrors and apertures to get smoother spectral baselines. Preliminary testing of the spectrometer at the end of this grant period indicated that this effort was successful.

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